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SIMULATION OF EDGE EFFECTS IN ELECTROANALYTICAL EXPERIMENTS BY --ETC(11)

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Part II. The Theory for Cyclic Voltammetry by Collocation.

Bernd Speiser and Stanley Pons

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The procedure and theory for simulation of currents perturbed by edge effects at disc electrodes in cyclic voltammetric experiments is presented. The results are obtained rapidly and accurately.		

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SIMULATION OF EDGE EFFECTS IN ELECTROANALYTICAL EXPERIMENTS  
BY ORTHOGONAL COLLOCATION. PART 1. THEORY FOR  
CYCLIC VOLTAMMETRY

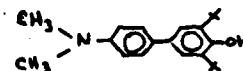
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INTRODUCTION

We have shown (1,2) that orthogonal collocation is suitable not only for the solution of linear diffusion problems but also for simulation of two-dimensional models. Thus, it is possible to simulate edge effects on electroanalytical experiments using this fast and flexible numerical technique.

Cyclic voltammetry is one of the most commonly used electroanalytical methods and it might be of considerable interest to calculate the effects caused by edge diffusion on the  $i/E$ -curves. Lines and Parker (3) have observed an increase of  $\Delta E_p$  when using microelectrodes and attributed this to edge effects, a conclusion which was confirmed by theoretical calculations by Heinze (4). Speiser and Rieker (5) found dramatic changes in cyclic voltammograms of 2,6-di-*tert*-butyl-4[4-dimethylaminophenyl]-phenol I in unbuffered, neutral acetonitrile when decreasing the electrode area from 0.29 cm<sup>2</sup> to 0.0022 cm<sup>2</sup>. These experiments have also been explained in terms of edge diffusion. Up to now, however, it was not possible to simulate the complex mechanism describing the oxidation of I under the conditions of a finite circular disc electrode.



This paper expands the theory of two-dimensional orthogonal collocation to cyclic voltammetry and mechanisms as complex as the oxidation of I. It will only deal with the mathematics of the method, while a complete numerical analysis showing the usefulness of the derived equations will be given in part 4.

This partition has been used because the analysis (which has to be done to validate the new two-dimensional collocation method) requires the discussion of many parameters. We point out, however, that this has to be done only once, while extension to more complicated mechanisms is obvious. Also, research on a comparison of the experimental results with 1 and numerical simulations is under way.

#### INITIAL AND BOUNDARY CONDITIONS

The initial and boundary conditions have been given by Nicholson and Shain (6) and used by Spelzer and Rieker (7) in the context of orthogonal collocation for linear diffusion. Pons (8) simulated cyclic voltammograms under spherical diffusion conditions using orthogonal collocation.

For simulation of edge effects we employ our two-dimensional model of a finite, circular electrode of radius  $r_0$  imbedded into an insulator body (1). The radius of the insulator may go to infinity.

We assume an EC mechanism:



where the diffusion controlled electron transfer is described by the formal potential,  $E^\circ$ , and the number of transferred electrons,  $n$ . The chemical step (2) proceeds with a rate constant  $k$ .

Fick's second law for the substrate A takes the form

$$\frac{\partial c_A}{\partial t} = D \left[ \frac{\partial^2 c_A}{\partial x^2} + \frac{1}{r} \frac{\partial c_A}{\partial r} + \frac{\partial^2 c_A}{\partial r^2} \right] \quad (3)$$

where  $t$  is time and  $x$  and  $r$  are the distance coordinate perpendicular to the electrode and the radial coordinate respectively. The total diffusion is expressed as superimposition of a linear and a cylindrical term.

For species B and C equations (4) and (5) hold:

$$\frac{\partial c_B}{\partial t} = D \left[ \frac{\partial^2 c_B}{\partial x^2} + \frac{1}{r} \frac{\partial c_B}{\partial r} + \frac{\partial^2 c_B}{\partial r^2} \right] - k c_B \quad (4)$$

$$\frac{\partial c_C}{\partial t} = D \left[ \frac{\partial^2 c_C}{\partial x^2} + \frac{1}{r} \frac{\partial c_C}{\partial r} + \frac{\partial^2 c_C}{\partial r^2} \right] + k c_B \quad (5)$$

For convenience the diffusion coefficient of all species is set equal to  $D$ .

We assume that A is the only species present in the solution at the beginning of the experiment, its concentration being  $c_A^\circ$ . Thus, the initial conditions are

$$t=0, x \geq 0, r \geq 0: \quad c_A(x, r, 0) = c_A^\circ \quad (6)$$

$$c_B(x, r, 0) = c_C(x, r, 0) = 0 \quad (7)$$

At a distance far from the electrode no concentration changes take place during the experiment. This yields the boundary conditions at  $x \rightarrow \infty$  and  $r \rightarrow \infty$

$$t > 0, x \rightarrow \infty, r \geq 0: \quad c_A(\infty, r, t) = c_A^\circ \quad (8)$$

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$$c_2(\infty, r, t) = c_2(\infty, r, t) = 0 \quad (9)$$

$$t > 0, x > 0, r \rightarrow \infty: \quad c_A(x, \infty, t) \rightarrow c_A^0 \quad (10)$$

$$c_2(x, \infty, t) = c_2(x, \infty, t) = 0 \quad (11)$$

At the electrode surface the concentrations of A and B are given by (12) and (13), while (14) holds for species C:

$$t > 0, x = 0, 0 \leq r \leq r_0: \quad \left( \frac{\partial c_A}{\partial x} \right)_{x=0} = - \left( \frac{\partial c_B}{\partial x} \right)_{x=0} \quad (12)$$

$$\frac{c_A(0, r, t)}{c_B(0, r, t)} = \exp \left[ \frac{nF}{RT} (E^0 - E) \right] = \theta_{A/B} S_A(t) \quad (13)$$

$$\left( \frac{\partial c_C}{\partial x} \right)_{x=0} = 0 \quad (14)$$

Equation (13) reflects the special features of cyclic voltammetry if

$$\theta_{A/B} = \exp \left[ \frac{nF}{RT} (E^0 - E_{start}) \right] \quad (15)$$

and

$$S_A(t) = \begin{cases} \exp[2(m-1)\alpha t_\lambda - \alpha t] & \text{for } 2(m-1)t_\lambda \leq t \leq 2m t_\lambda \\ \exp[\alpha t - 2m \alpha t_\lambda] & \text{for } (2m-1)t_\lambda \leq t \leq 2m t_\lambda \end{cases} \quad m=1, 2, \dots \quad (16)$$

Here  $F$ ,  $R$  and  $T$  have their usual meaning,  $E_{start}$  is the starting potential of the scan,  $t$  the time when the scan is reversed,  $m$  the number of the present scan. A cycle consists of two scans. Finally  $\alpha$  is given by

$$\alpha = \frac{nF}{RT} v \quad (17)$$

where  $v$  is the scan rate,  $dE/dt$ .

There is no redox reaction at the insulator and hence no flux through this surface. Thus

$$t > 0, x = 0, r \gg r_0:$$

$$\left( \frac{\partial c_A}{\partial x} \right)_{x=0} = \left( \frac{\partial c_B}{\partial x} \right)_{x=0} = \left( \frac{\partial c_C}{\partial x} \right)_{x=0} = 0 \quad (18)$$

At  $r = 0$  there must be no flux in  $r$ -direction because our model is symmetric around  $r = 0$ :

$$t > 0, x \gg 0, r = 0:$$

$$\left( \frac{\partial c_A}{\partial r} \right)_{r=0} = \left( \frac{\partial c_B}{\partial r} \right)_{r=0} = \left( \frac{\partial c_C}{\partial r} \right)_{r=0} = 0 \quad (19)$$

It is convenient [1] to divide the space in the  $r$ -direction into two parts, inside and outside of  $r_0$ . The concentration may be described by  $c_1$  and  $c_2$ , respectively. The two concentration

functions have to fulfill the conditions (20) and (21) at  $r = r_0$  for all species.

$t > 0, x \geq 0, r = r_0$ :

$$c_1(x, r_0, t) = c_2(x, r_0, t) \quad (20)$$

$$\left( \frac{\partial c_1}{\partial r} \right)_{r=r_0} = \left( \frac{\partial c_2}{\partial r} \right)_{r=r_0} \quad (21)$$

#### TRANSFORMATION TO A DIMENSIONLESS PROBLEM

Equations (3)-(22) are transformed into a dimensionless problem by

$$X = x/L \quad (22)$$

$$c_{A1}^* = c_{A1}/c_A^0 \quad (23)$$

$$c_{A2}^* = c_{A2}/c_A^0 \quad (24)$$

$$c_{B1}^* = c_{B1}/c_A^0 \quad (25)$$

$$c_{B2}^* = c_{B2}/c_A^0 \quad (26)$$

$$c_{C1}^* = c_{C1}/c_A^0 \quad (27)$$

$$c_{C2}^* = c_{C2}/c_A^0 \quad (28)$$

$$R = r/r_0 \quad \text{for } 0 \leq r \leq r_0 \quad (29a)$$

$$R = (r - r_0)/(R - r_0) \quad \text{for } r \geq r_0 \quad (29b)$$

$$T' = at \quad (30)$$

$$\alpha = kD/r_0^2 \quad (31)$$

Here  $X$  is a dimensionless distance perpendicular to the electrode,  $L$  is a distance from the electrode defined such that diffusion effects are negligible at all times the  $c^0$  are dimensionless concentrations,  $R$  and  $R'$  are dimensionless coordinates in  $r$ -direction for the inner and outer functions respectively, while  $M$  is defined as  $L$  except it is a radial distance from the center of the electrode. The symbols  $T'$  and  $a$  denote the dimensionless simulation time and rate constant respectively.

Thus, we get the dimensionless differential equations:

$$\frac{\partial c_{A1}^*}{\partial T'} = \beta \frac{\partial^2 c_{A1}^*}{\partial X^2} + \frac{\beta'}{R} \frac{\partial c_{A1}^*}{\partial R} + \beta' \frac{\partial^2 c_{A1}^*}{\partial R^2} \quad (32)$$

$$\frac{\partial c_{B1}^*}{\partial T'} = \beta \frac{\partial^2 c_{B1}^*}{\partial X^2} + \frac{\beta'}{R} \frac{\partial c_{B1}^*}{\partial R} + \beta' \frac{\partial^2 c_{B1}^*}{\partial R^2} - \alpha c_{B1}^* \quad (33)$$

$$\frac{\partial c_{A1}^*}{\partial T'} = \beta \frac{\partial^2 c_{A1}^*}{\partial X^2} + \frac{\beta'}{R} \frac{\partial c_{A1}^*}{\partial R} + \beta'' \frac{\partial^2 c_{A1}^*}{\partial R^2} + \alpha c_{A1}^* \quad (34)$$

$$\frac{\partial c_{A2}^*}{\partial T'} = \beta \frac{\partial^2 c_{A2}^*}{\partial X^2} + \frac{\sqrt{\beta'} \beta''}{\sqrt{\beta''} + \sqrt{\beta'} R'} \frac{\partial c_{A2}^*}{\partial R} + \beta'' \frac{\partial^2 c_{A2}^*}{\partial R^2} \quad (35)$$

$$\frac{\partial c_{B1}^*}{\partial T'} = \beta \frac{\partial^2 c_{B1}^*}{\partial X^2} + \frac{\sqrt{\beta'} \beta''}{\sqrt{\beta''} + \sqrt{\beta'} R'} \frac{\partial c_{B1}^*}{\partial R} + \beta'' \frac{\partial^2 c_{B1}^*}{\partial R^2} - \alpha c_{B1}^* \quad (36)$$

$$\frac{\partial c_{B2}^*}{\partial T'} = \beta \frac{\partial^2 c_{B2}^*}{\partial X^2} + \frac{\sqrt{\beta'} \beta''}{\sqrt{\beta''} + \sqrt{\beta'} R'} \frac{\partial c_{B2}^*}{\partial R} + \beta'' \frac{\partial^2 c_{B2}^*}{\partial R^2} + \alpha c_{B2}^* \quad (37)$$

where  $\beta$  is given by

$$\beta = D/aL^2 \quad (38)$$

$\beta'$  contains only experimental parameters

$$\beta' = D/a\tau_0^2 \quad (39)$$

and

$$\beta'' = D/a(N-\tau_0)^2 \quad (40)$$

As in the case of the chronoamperometric simulations [1] we have

two dimensionless parameters, here  $\beta$  and  $\beta''$ . The parameter  $\beta'$  is given by experimental parameters and thus the simulations will depend on  $\beta'$  as e.g. on  $\alpha$ .

The transformed initial and boundary conditions are given

by

$$T'=0, 0 \leq X \leq 1, 0 \leq R \leq 1, 0 \leq R' \leq 1: \quad c_{A1}^*(X, R, 0) = c_{A2}^*(X, R', 0) = 1 \quad (41)$$

$$c_{B1}^*(X, R, 0) = c_{B2}^*(X, R', 0) =$$

$$c_{A1}^*(X, R, 0) = c_{B1}^*(X, R', 0) = 0 \quad (42)$$

$$T' > 0, X=1, 0 \leq R \leq 1;$$

$$c_{A1}^*(1, R, T') = 1 \quad (43)$$

$$c_{B1}^*(1, R, T') = c_{B2}^*(1, R', T') = 0 \quad (44)$$

$$T' > 0, X=1, 0 \leq R' \leq 1:$$

$$c_{A2}^*(1, R', T') = 1 \quad (45)$$

$$c_{B2}^*(1, R', T') = c_{B1}^*(1, R, T') = 0 \quad (46)$$

$$T' > 0, 0 \leq X \leq 1, R=1:$$

$$c_{A1}^*(X, 1, T') = 1 \quad (47)$$

$$c_{B1}^*(X, 1, T') = c_{B2}^*(X, 1, T') = 0 \quad (48)$$

$$T' > 0, X=0, 0 \leq R \leq 1:$$

$$\left( \frac{\partial c_{A1}^*}{\partial X} \right)_{X=0} = - \left( \frac{\partial c_{B1}^*}{\partial X} \right)_{X=0} \quad (49)$$

$$\frac{c_{A0}^*(0, R, T')}{c_{A0}^*(0, R, T')} = \Theta_{A/B} S_A(T') \quad (50)$$

with

$$S_A(T') = \begin{cases} \exp[2(m-1)T'_A - T'] \\ \exp[T' - 2mT'_A] \end{cases} \quad m = 1, 2, \dots \quad (51)$$

where

$$T'_A = \alpha t_A \quad (52)$$

$$\left( \frac{\partial c_{A1}^*}{\partial x} \right)_{x=0} = 0 \quad (53)$$

$$T' > 0, x=0, 0 < R' \leq 1: \quad \left( \frac{\partial c_{A1}^*}{\partial x} \right)_{x=0} = \left( \frac{\partial c_{B1}^*}{\partial x} \right)_{x=0} = \left( \frac{\partial c_{C1}^*}{\partial x} \right)_{x=0} = 0 \quad (54)$$

$$T' > 0, 0.6 \leq R' \leq 1, R=0: \quad \left( \frac{\partial c_{A1}^*}{\partial R} \right)_{R=0} = \left( \frac{\partial c_{B1}^*}{\partial R} \right)_{R=0} = \left( \frac{\partial c_{C1}^*}{\partial R} \right)_{R=0} = 0 \quad (55)$$

$$T' > 0, 0 \leq x \leq 1, R=1 (R'=0): \quad c_{A1}^*(x, 1, T') = c_{A1}^*(x, 0, T') \quad (56)$$

$$c_{B1}^*(x, 1, T') = c_{B1}^*(x, 0, T') \quad (57)$$

$$c_{A1}^*(x, 1, T') = c_{A1}^*(x, 0, T') \quad (58)$$

$$\left( \frac{\partial c_{A1}^*}{\partial R} \right)_{R=1} = \sqrt{\frac{A'}{N}} \left( \frac{\partial c_{A1}^*}{\partial R'} \right)_{R'=0} \quad (59)$$

$$\left( \frac{\partial c_{B1}^*}{\partial R} \right)_{R=1} = \sqrt{\frac{A'}{N}} \left( \frac{\partial c_{B1}^*}{\partial R'} \right)_{R'=0} \quad (60)$$

$$\left( \frac{\partial c_{C1}^*}{\partial R} \right)_{R=1} = \sqrt{\frac{A'}{N}} \left( \frac{\partial c_{C1}^*}{\partial R'} \right)_{R'=0} \quad (61)$$

## APPLICATION OF TWO-DIMENSIONAL COLLOCATION

As in the case of chronoamperometry [1] we have to solve the system of second order partial differential equations (32)-(37) under the conditions (41)-(61) to get the dimensionless concentrations of species A, B and C as functions of  $x$ ,  $R$  ( $R'$ ) and  $T'$ . We use the two-dimensional collocation method outlined in part I of this series [1] to discretize equations (32)-(37) with respect to the grid of collocation points ( $x_i$ ,  $R_k$ ) in the  $x/R$ -space.

We have shown [1] that the first and second derivatives of the concentration with respect to  $x$  and  $r$  respectively at a collocation point ( $x_i$ ,  $R_k$ ) may be expressed as

$$\left( \frac{\partial c}{\partial x} \right)_{x_i, R_k} = \sum_{j=1}^{M_x+2} A_{ij} c(x_j, r_k, t) \quad (62)$$



$$\left(\frac{\partial^2 c}{\partial x^2}\right)_{x_i, r_R} = \sum_{j=2}^{N_x+2} B_{i,j} c(x_j, r_R, t) \quad (63)$$

$$\left(\frac{\partial c}{\partial r}\right)_{x_i, r_R} = \sum_{e=2}^{N_r+2} C_{e,k} c(x_i, r_e, t) \quad (64)$$

$$\left(\frac{\partial^2 c}{\partial r^2}\right)_{x_i, r_R} = \sum_{e=2}^{N_r+2} D_{e,k} c(x_i, r_e, t) \quad (65)$$

where  $N_x$  and  $N_r$  are the numbers of interior collocation points (chosen as the roots of an orthogonal polynomial [9]) in the  $x$  and  $r$  direction respectively and  $A_{i,j}$ ,  $B_{i,j}$ ,  $C_{i,k}$  and  $D_{i,k}$  are elements of matrices. The numerical values of those elements depend only on the degree and kind of the polynomial chosen for collocation [10]. Thus, if the matrix elements have once been calculated they may be used for any problem. The degree of the polynomial used depends on the desired accuracy of the simulation.

Using equations (62)-(65) we may discretize the partial differential equations (32)-(37) in terms of the concentrations at the collocation points. If we introduce the boundary conditions (43)-(48) we arrive at equations (66)-(71).

$$\frac{dc_{A2}}{dT'} \bigg|_{x_i, r_R} = \beta \left\{ B_{i,1} c_{A2}^0(0, r_R, T') + B_{i, N_x+2} + \sum_{j=2}^{N_x+2} B_{i,j} c_{A2}^0(x_j, r_R, T') \right\} \\ + \beta' \left\{ E_{i,1} c_{A2}^0(x_i, 0, T') + E_{i, N_r+2} c_{A2}^0(x_i, r_R, T') + \sum_{e=2}^{N_r+2} E_{e,k} c_{A2}^0(x_i, r_e, T') \right\} \quad (66)$$

$$\frac{dc_{B1}}{dT'} \bigg|_{x_i, r_R} = \beta \left\{ B_{i,1} c_{B1}^0(0, r_R, T') + \sum_{j=2}^{N_x+2} B_{i,j} c_{B1}^0(x_j, r_R, T') \right\} \\ + \beta' \left\{ E_{i,1} c_{B1}^0(x_i, 0, T') + E_{i, N_r+2} c_{B1}^0(x_i, r_R, T') + \sum_{e=2}^{N_r+2} E_{e,k} c_{B1}^0(x_i, r_e, T') \right\} - c_{B1}^0 \quad (67)$$

$$\frac{dc_{A4}}{dT'} \bigg|_{x_i, r_R} = \beta \left\{ B_{i,1} c_{A4}^0(0, r_R, T') + \sum_{j=2}^{N_x+2} B_{i,j} c_{A4}^0(x_j, r_R, T') \right\} \\ + \beta' \left\{ E_{i,1} c_{A4}^0(x_i, 0, T') + E_{i, N_r+2} c_{A4}^0(x_i, r_R, T') + \sum_{e=2}^{N_r+2} E_{e,k} c_{A4}^0(x_i, r_e, T') \right\} + c_{A4}^0 \quad (68)$$

$$\frac{dc_{B2}}{dT'} \bigg|_{x_i, r_R} = \beta \left\{ B_{i,1} c_{B2}^0(0, r_R, T') + B_{i, N_x+2} + \sum_{j=2}^{N_x+2} B_{i,j} c_{B2}^0(x_j, r_R, T') \right\} \\ + \beta' \left\{ F_{i,1} c_{B2}^0(x_i, 0, T') + F_{i, N_r+2} c_{B2}^0(x_i, r_R, T') + \sum_{e=2}^{N_r+2} F_{e,k} c_{B2}^0(x_i, r_e, T') \right\} \quad (69)$$

$$\frac{dc_{B7}}{dT'} \bigg|_{x_i, r_R} = \beta \left\{ B_{i,1} c_{B7}^0(0, r_R, T') + \sum_{j=2}^{N_x+2} B_{i,j} c_{B7}^0(x_j, r_R, T') \right\} \\ + \beta' \left\{ F_{i,1} c_{B7}^0(x_i, 0, T') + \sum_{e=2}^{N_r+2} F_{e,k} c_{B7}^0(x_i, r_e, T') \right\} - c_{B7}^0 \quad (70)$$

$$\frac{dc_{21}^0}{dT} = \beta \left\{ B_{2,1} c_{21}^0(0, R_A, T') + \sum_{j=2}^{N_{2,1}+1} B_{2,j} c_{21}^0(x_j, R_A, T') \right\} \quad (71)$$

$$+ \beta^0 \left\{ F'_{1,A} c_{21}^0(x_1, 0, T') + \sum_{e=2}^{N_{e,1}+1} F'_{e,A} c_{21}^0(x_e, R_e, T') \right\} + \alpha c_{21}^0$$

with

$$E_{e,A} = \frac{C_{e,A} + R_A D_{e,A}}{R_A} \quad (72)$$

and

$$F'_{e,A} = \frac{\sqrt{R'}}{\sqrt{R'} + \sqrt{R'_A} R'_A} C'_{e,A} + D'_{e,A} \quad (73)$$

Primed matrix elements correspond to the outer discretization function. As in the case of chronoamperometry we have to substitute implicit equations for the unknown concentrations at the boundaries. The calculations of the  $c_1^0(x_1, 0, T')$ ,  $c_1^0(x_1, 1, T')$ ,  $c_2^0(x_1, 0, T')$ ,  $c_1^0(0, R_A, T')$  and  $c_2^0(0, R_A, T')$  is essentially the same as for chronoamperometric simulations and we refer to part 1 of this series [1] for the derivations.

They are [1]:

$$c_{A,1}^0(x_1, 0, T') = -\frac{1}{G_1} \left\{ \sum_{e=2}^{N_{e,1}+1} G_e c_{A,1}^0(x_1, R_e, T') + \sum_{e=2}^{N_{e,1}+1} C_{N_{e,1}+1,e} C'_{e,A} c_{A,1}^0(x_1, R_e, T') + C_{N_{e,1}+1,1} C'_{N_{e,1}+1,A} \right\} \quad (74)$$

$$c_{B,2}^0(x_1, 0, T') = -\frac{1}{G_1} \left\{ \sum_{e=2}^{N_{e,1}+1} G_e c_{B,2}^0(x_1, R_e, T') + \sum_{e=2}^{N_{e,1}+1} C_{N_{e,1}+1,e} C'_{e,A} c_{B,2}^0(x_1, R_e, T') \right\} \quad (75)$$

$$c_{C,2}^0(x_1, 0, T') = -\frac{1}{G_1} \left\{ \sum_{e=2}^{N_{e,1}+1} G_e c_{C,2}^0(x_1, R_e, T') + \sum_{e=2}^{N_{e,1}+1} C_{N_{e,1}+1,e} C'_{e,A} c_{C,2}^0(x_1, R_e, T') \right\} \quad (76)$$

$$c_{A,1}^0(x_1, 1, T') = c_{A,1}^0(x_1, 0, T') = \frac{1}{G_2} \left\{ \sum_{e=2}^{N_{e,1}+1} H_e c_{A,1}^0(x_1, R_e, T') + \sum_{e=2}^{N_{e,1}+1} C_{1,e} C'_{e,A} c_{A,1}^0(x_1, R_e, T') + C_{1,A} C'_{N_{e,1}+1,A} \right\} \quad (77)$$

$$c_{B,2}^0(x_1, 1, T') = c_{B,2}^0(x_1, 0, T') = \frac{1}{G_2} \left\{ \sum_{e=2}^{N_{e,1}+1} H_e c_{B,2}^0(x_1, R_e, T') + \sum_{e=2}^{N_{e,1}+1} C_{1,e} C'_{e,A} c_{B,2}^0(x_1, R_e, T') \right\} \quad (78)$$

$$c_{e0}^*(x_i, t, T) = c_{e1}^*(x_i, 0, T') = \frac{1}{G_e} \left\{ \sum_{e=2}^{N_{e+1}} H_e c_{e0}^*(x_i, R_e, T) + \sum_{e=2}^{N_{e+1}} C_{e0} C_{e,1}' c_{e1}^*(x_i, R_e, T') \right\} \quad (79)$$

$$c_{e1}^*(0, R_e, T) = -\frac{1}{A_{e+1}} \sum_{j=2}^{N_{e+1}} A_{e,j} c_{e1}^*(x_j, R_e, T') \quad (80)$$

$$c_{a1}^*(0, R_a, T') = -\frac{1}{A_{a+1}} \left\{ A_{a, N_{a+2}} + \sum_{j=2}^{N_{a+1}} A_{a,j} c_{a1}^*(x_j, R_a, T') \right\} \quad (81)$$

$$c_{b1}^*(0, R_b, T') = -\frac{1}{A_{b+1}} \sum_{j=2}^{N_{b+1}} A_{b,j} c_{b1}^*(x_j, R_b, T') \quad (82)$$

$$c_{c1}^*(0, R_c, T') = -\frac{1}{A_{c+1}} \sum_{j=2}^{N_{c+1}} A_{c,j} c_{c1}^*(x_j, R_c, T') \quad (83)$$

with

$$G_e = (C_{N_{e+1}, N_{e+1}} - C_{e,1}') C_{e,1} - C_{e, N_{e+2}} C_{N_{e+1}, e} \quad (84)$$

and

$$H_e = C_{a, N_{a+2}} C_{e,1} - C_{e,1} C_{e, N_{e+2}} \quad (85)$$

The values of  $c_{a1}^*(0, R_a, T')$  and  $c_{b1}^*(0, R_b, T')$  may be calculated from equations (49) and (50), yielding

$$c_{a1}^*(0, R_a, T') = -\frac{\theta_{a/B} S_a(T')}{A_{a+1} [1 + \theta_{a/B} S_a(T')]} \times \left\{ A_{a, N_{a+2}} + \sum_{j=2}^{N_{a+1}} A_{a,j} [c_{a1}^*(x_j, R_a, T') + c_{b1}^*(x_j, R_a, T')] \right\} \quad (86)$$

and

$$c_{b1}^*(0, R_b, T') = -\frac{1}{A_{b+1} [1 + \theta_{a/B} S_a(T')]} \times \left\{ A_{b, N_{b+2}} + \sum_{j=2}^{N_{b+1}} A_{b,j} [c_{a1}^*(x_j, R_b, T') + c_{b1}^*(x_j, R_b, T')] \right\} \quad (87)$$

Now we may substitute (74)-(87) into equations (66)-(71) which gives us finally the discretized equations describing the time dependence of the concentration of all three species A, B and C at the collocation points.

From (66) it follows using (74), (77) and (86)

$$\begin{aligned} \frac{dc_{A,2}}{dT'} \bigg|_{X_i, R_0} = & \beta \left\{ - \frac{B_{i,2} \Theta_{A,2} c_{A,2}(T')}{A_{i,2} [1 + \Theta_{A,2} S_2(T')]} \left[ A_{i,2} \mu_{2,2} + \sum_{j=2}^{N_{A,2}} A_{i,j} [c_{A,2}^*(X_i, R_0, T') \right. \right. \\ & \left. \left. + c_{A,2}^*(X_j, R_0, T') \right] + B_{i,2} \mu_{2,2} + \sum_{j=2}^{N_{A,2}} B_{i,j} c_{A,2}^*(X_j, R_0, T') \right\} \\ & + \frac{\beta'}{G_1} \left\{ I_{i,2} C_{A,2}^* + \sum_{e=2}^{N_{A,2}} [I_{e,2} (C_{i,2}' - C_{A,2} \mu_{2,2}) - I_{e,2} C_{e,2} \mu_{2,2} - I_{e,2} C_{A,2} \mu_{2,2}] \right. \\ & \left. \cdot c_{A,2}^*(X_i, R_0, T') + \sum_{e=2}^{N_{A,2}} I_{e,2} C_{e,2}' c_{A,2}^*(X_i, R_0, T') \right\} \end{aligned} \quad (88)$$

where

$$I_{e,2} = E_{A,2,2,2} C_{e,2} - E_{e,2} C_{A,2,2,2} \quad (89)$$

and

$$J_{e,2} = E_{i,2} C_{e,2} - E_{e,2} C_{i,2} \quad (90)$$

If we combine (67) with (75), (78) and (87), we get

$$\begin{aligned} \frac{dc_{A,2}}{dT'} \bigg|_{X_i, R_0} = & \beta \left\{ - \frac{B_{i,2}}{A_{i,2} [1 + \Theta_{A,2} S_2(T')]} \left[ A_{i,2} \mu_{2,2} + \sum_{j=2}^{N_{A,2}} A_{i,j} [c_{A,2}^*(X_i, R_0, T') + c_{A,2}^*(X_j, R_0, T')] \right] \right. \\ & \left. + \sum_{j=2}^{N_{A,2}} B_{i,j} c_{A,2}^*(X_j, R_0, T') \right\} + \frac{\beta'}{G_1} \left\{ \sum_{e=2}^{N_{A,2}} [I_{e,2} (C_{i,2}' - C_{A,2} \mu_{2,2}) - I_{e,2} C_{e,2} \mu_{2,2} \right. \\ & \left. - I_{e,2} C_{A,2} \mu_{2,2}] c_{A,2}^*(X_i, R_0, T') + \sum_{e=2}^{N_{A,2}} I_{e,2} C_{e,2}' c_{A,2}^*(X_i, R_0, T') \right\} - \alpha c_{A,2}^* \end{aligned} \quad (91)$$

similarly (68) gives with (76), (79) and (80)

$$\begin{aligned} \frac{dc_{A,2}}{dT'} \bigg|_{X_i, R_0} = & \frac{\beta}{A_{i,2}} \sum_{j=2}^{N_{A,2}} K_{i,j} c_{A,2}^*(X_j, R_0, T') \\ & + \frac{\beta'}{G_1} \left\{ \sum_{e=2}^{N_{A,2}} [I_{e,2} (C_{i,2}' - C_{A,2} \mu_{2,2}) - I_{e,2} C_{e,2} \mu_{2,2} - I_{e,2} C_{A,2} \mu_{2,2}] c_{A,2}^*(X_i, R_0, T') \right. \\ & \left. + \sum_{e=2}^{N_{A,2}} I_{e,2} C_{e,2}' c_{A,2}^*(X_i, R_0, T') \right\} + \alpha c_{A,2}^* \end{aligned} \quad (92)$$

For the outer function describing the concentration

species A it holds from (69), (77), and (81)

$$\begin{aligned} \frac{dc_{A,2}}{dT'} \bigg|_{X_i, R_0} = & \frac{\beta}{A_{i,2}} \left\{ K_{i,2} \mu_{2,2} + \sum_{j=2}^{N_{A,2}} K_{i,j} c_{A,2}^*(X_j, R_0, T') \right\} \\ & + \frac{\beta'}{G_1} \left\{ L_{i,2} \mu_{2,2} + \sum_{e=2}^{N_{A,2}} L_{e,2} H_{e,2} c_{A,2}^*(X_i, R_0, T') + \sum_{e=2}^{N_{A,2}} L_{e,2}' c_{A,2}^*(X_i, R_0, T') \right\} \end{aligned} \quad (93)$$

Equations (70), (78), and (82) combine to give

$$\begin{aligned} \frac{dc_{A,2}}{dT'} \bigg|_{X_i, R_0} = & \frac{\beta}{A_{i,2}} \sum_{j=2}^{N_{A,2}} K_{i,j} c_{A,2}^*(X_j, R_0, T') \\ & + \frac{\beta'}{G_1} \left\{ \sum_{e=2}^{N_{A,2}} F_{e,2} H_{e,2} c_{A,2}^*(X_i, R_0, T') + \sum_{e=2}^{N_{A,2}} L_{e,2}' c_{A,2}^*(X_i, R_0, T') \right\} - \alpha c_{A,2}^* \end{aligned} \quad (94)$$

Finally (71), (79), and (83) yield

$$\frac{dc_{c2}^*}{dT} = \frac{\beta}{x_i R_i} \sum_{j=2}^{N_{c2}} K_{c2j} c_{c2}^* (x_i, R_i, T) + \frac{\beta}{G_i} \left[ \sum_{j=2}^{N_{c2}} F'_{c2j} H_{c2j} c_{c2}^* (x_i, R_i, T) + \sum_{j=2}^{N_{c2}} L'_{c2j} c_{c2}^* (x_i, R_i, T) \right] + \alpha c_{c2}^* \quad (95)$$

where we used

$$K_{c2j} = B_{c2j} A_{c2j} - B_{c2j} A_{c2j} \quad (96)$$

and

$$L'_{c2j} = F'_{c2j} G_i + C_{c2j} C'_{c2j} F'_{c2j} \quad (97)$$

Thus, the system of 6 second order partial differential equations (32)-(37) has been converted into a set of  $3N_x(N_R + N_R)$  simultaneous ordinary differential equations, (88) and (91)-(95). After integrating this set we get the concentrations of species A, B and C at the collocation points  $(x_i, R_k)$  and  $(x_i, R_k')$  as a function of the simulation time  $T$ .

One of the distinctive features of the orthogonal collocation approach can be seen from a comparison of equations (88) and (91)-(95). Those formulae are very similar from a structural point of view. Furthermore, compared to the expressions describing the model of a chronoamperometric experiment [1], there are only few changes in the inner

functions, while the outer functions are the same both for the models of cyclic voltammetry and chronoamperometry.

#### CALCULATION OF THE CURRENT

Also, the calculation of the current is fully analogous to that performed for the chronoamperometric model. Again we have to integrate the flux over the part between 0 and  $r_0$  on the  $r$ -axis

$$i = nFD \int_0^{r_0} 2\pi r \left( \frac{\partial c_A}{\partial x} \right)_{x=0} dr \quad (98)$$

Transforming the right hand side of equation (98) into a dimensionless form we get

$$i = nFAc_A^* \sqrt{D\alpha\pi} \sqrt{\frac{r_0}{\pi}} \cdot 2 \int_0^1 R \left( \frac{\partial c_A}{\partial X} \right)_{X=0} dR \quad (99)$$

or, using Nicholson and Shain's current function [6]

$$\chi = \frac{i}{nFAc_A^* \sqrt{D\alpha\pi}} = 2 \sqrt{\frac{\beta}{\pi}} \int_0^1 R \left( \frac{\partial c_A}{\partial X} \right)_{X=0} dR \quad (100)$$

The integration may be performed exactly by a quadrature method [11], for we know the derivative  $(\partial c_A / \partial X)_{X=0}$  at all collocation points

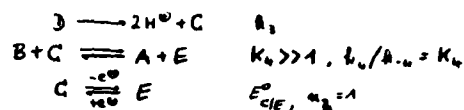
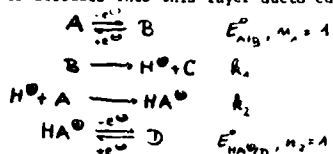
$$\chi = 2\sqrt{\frac{\beta}{\pi}} \sum_{i=1}^{N_{i+2}} Q_i R_i \frac{1}{1 + \frac{1}{2} \frac{A}{S_A(r)}} - [A_{i+1}, \mu_i, \nu_i]^+ \quad (101)$$

$$\sum_{j=2}^{N_{i+4}} A_{ij} c_{A_i}^*(x_j, R_i, T') - \theta_{A/B} S_A(r) \sum_{j=2}^{N_{i+4}} A_{ij} c_{B_i}^*(x_j, R_i, T')$$

where the elements of the vector  $Q$  depend only on the degree and kind of the trial function in  $x$ -direction.

#### MODEL MECHANISM FOR OXIDATION OF I

It has been shown [12,13] that the oxidation of I (denoted as A) may be described by an ECE-type mechanism, where protons released after the oxidation step are picked up by unoxidized phenol molecules giving the protonated form of I,  $HA^+$ . The latter is oxidized at more positive potentials releasing two protons during reaction. The end product of both reactions is the stable phenoxonium cation, E, which is most probably formed from the neutral phenoxy radical, C, in a homogeneous redox reaction between C and the primary radical cation B [13]. The intermediate D was not oxidized further. The observation of changes in voltammograms of I with electrode size has been attributed to the protonation reaction  $A \rightarrow HA^+$  which causes a phenol-free layer in front of the electrode [5]. The time after which phenol again reaches the electrode surface is decreased if more substrate diffuses into this layer due to edge effects.



With our two-dimensional simulation model it is now possible to include the effects of a finite disc into the calculations. This may also serve as a further example for the application of orthogonal collocation to electroanalytical problems. In this paper we show the derivation of the expressions for  $dc^*/dt'$  for the species involved, while the comparison with experimental results will be reported in part 4 of this series.

The kinetic diffusion equations for the above model mechanism in dimensionless form are

$$\frac{\partial c_{A_i}^*}{\partial t'} = \beta \frac{\partial^2 c_{A_i}^*}{\partial x^2} + \frac{\beta'}{R} \frac{\partial c_{A_i}^*}{\partial R} + \beta' \frac{\partial^2 c_{A_i}^*}{\partial R^2} - \alpha_1 c_{A_i}^* c_{B_i}^* - \alpha_2 c_{A_i}^* c_{C_i}^* + \alpha_3 c_{B_i}^* c_{C_i}^* \quad (102)$$

$$\frac{\partial c_{B_i}^*}{\partial t'} = \beta \frac{\partial^2 c_{B_i}^*}{\partial x^2} + \frac{\beta'}{R} \frac{\partial c_{B_i}^*}{\partial R} + \beta' \frac{\partial^2 c_{B_i}^*}{\partial R^2} - \alpha_1 c_{A_i}^* c_{B_i}^* - \alpha_2 c_{B_i}^* c_{C_i}^* + \alpha_3 c_{B_i}^* c_{C_i}^* \quad (103)$$

$$\frac{\partial c_{C_i}^*}{\partial t'} = \beta \frac{\partial^2 c_{C_i}^*}{\partial x^2} + \frac{\beta'}{R} \frac{\partial c_{C_i}^*}{\partial R} + \beta' \frac{\partial^2 c_{C_i}^*}{\partial R^2} + \alpha_1 c_{A_i}^* c_{B_i}^* + \alpha_2 c_{B_i}^* c_{C_i}^* - \alpha_3 c_{B_i}^* c_{C_i}^* + \alpha_4 c_{A_i}^* c_{C_i}^* \quad (104)$$

$$\frac{\partial c_{HA^+}^*}{\partial t'} = \beta \frac{\partial^2 c_{HA^+}^*}{\partial x^2} + \frac{\beta'}{R} \frac{\partial c_{HA^+}^*}{\partial R} + \beta' \frac{\partial^2 c_{HA^+}^*}{\partial R^2} + \alpha_1 c_{A_i}^* c_{B_i}^* + 2\alpha_2 c_{B_i}^* c_{C_i}^* - \alpha_3 c_{B_i}^* c_{C_i}^* \quad (105)$$

$$\frac{\partial c_{\mu\omega_2}}{\partial T'} = \beta \frac{\partial^2 c_{\mu\omega_2}}{\partial X^2} + \frac{\beta'}{R} \frac{\partial c_{\mu\omega_2}}{\partial R} + \beta'' \frac{\partial^2 c_{\mu\omega_2}}{\partial R^2} + \alpha_2 c_{\lambda_1}^* c_{\mu\omega_2}$$

(106)

$$\frac{\partial c_{\mu\omega_1}}{\partial T'} = \beta \frac{\partial^2 c_{\mu\omega_1}}{\partial X^2} + \frac{\beta'}{R} \frac{\partial c_{\mu\omega_1}}{\partial R} + \beta'' \frac{\partial^2 c_{\mu\omega_1}}{\partial R^2} - \alpha_3 c_{\lambda_2}^*$$

(107)

$$\frac{\partial c_{\mu\omega_2}}{\partial T'} = \beta \frac{\partial^2 c_{\mu\omega_2}}{\partial X^2} + \frac{\beta'}{R} \frac{\partial^2 c_{\mu\omega_2}}{\partial R} + \beta'' \frac{\partial^2 c_{\mu\omega_2}}{\partial R^2} + \alpha_2 c_{\mu\omega_2}^* c_{\lambda_1}^* - \alpha_4 c_{\lambda_1}^* c_{\mu\omega_2}$$

(108)

$$\frac{\partial c_{\lambda_2}^*}{\partial T'} = \beta \frac{\partial^2 c_{\lambda_2}^*}{\partial X^2} + \frac{\beta' \sqrt{R'}}{\sqrt{R''} + \sqrt{R'} R'} \frac{\partial c_{\lambda_2}^*}{\partial R'} + \beta'' \frac{\partial^2 c_{\lambda_2}^*}{\partial R'^2} - \alpha_2 c_{\mu\omega_2}^* c_{\lambda_1}^* - \alpha_4 c_{\lambda_1}^* c_{\mu\omega_2} + \alpha_5 c_{\mu\omega_1}^* c_{\lambda_2}^*$$

(109)

$$\frac{\partial c_{\lambda_1}^*}{\partial T'} = \beta \frac{\partial^2 c_{\lambda_1}^*}{\partial X^2} + \frac{\beta' \sqrt{R'}}{\sqrt{R''} + \sqrt{R'} R'} \frac{\partial c_{\lambda_1}^*}{\partial R'} + \beta'' \frac{\partial^2 c_{\lambda_1}^*}{\partial R'^2} - \alpha_1 c_{\mu\omega_1}^* - \alpha_5 c_{\mu\omega_1}^* c_{\lambda_2}^* + \alpha_6 c_{\mu\omega_1}^* c_{\lambda_1}^*$$

(110)

$$\frac{\partial c_{\lambda_1}^*}{\partial T'} = \beta \frac{\partial^2 c_{\lambda_1}^*}{\partial X^2} + \frac{\beta' \sqrt{R'}}{\sqrt{R''} + \sqrt{R'} R'} \frac{\partial c_{\lambda_1}^*}{\partial R'} + \beta'' \frac{\partial^2 c_{\lambda_1}^*}{\partial R'^2} + \alpha_1 c_{\mu\omega_1}^* + \alpha_5 c_{\mu\omega_1}^* - \alpha_6 c_{\mu\omega_1}^* c_{\lambda_1}^* + \alpha_7 c_{\lambda_1}^* c_{\mu\omega_1}^*$$

(111)

$$\frac{\partial c_{\mu\omega_2}}{\partial T'} = \beta \frac{\partial^2 c_{\mu\omega_2}}{\partial X^2} + \frac{\beta' \sqrt{R'}}{\sqrt{R''} + \sqrt{R'} R'} \frac{\partial c_{\mu\omega_2}}{\partial R'} + \beta'' \frac{\partial^2 c_{\mu\omega_2}}{\partial R'^2} + \alpha_2 c_{\mu\omega_2}^* + 2\alpha_3 c_{\mu\omega_2}^* - \alpha_4 c_{\lambda_1}^* c_{\mu\omega_2}^* \quad (112)$$

$$\frac{\partial c_{\mu\omega_2}}{\partial T'} = \beta \frac{\partial^2 c_{\mu\omega_2}}{\partial X^2} + \frac{\beta' \sqrt{R'}}{\sqrt{R''} + \sqrt{R'} R'} \frac{\partial c_{\mu\omega_2}}{\partial R'} + \beta'' \frac{\partial^2 c_{\mu\omega_2}}{\partial R'^2} + \alpha_2 c_{\lambda_1}^* c_{\mu\omega_2}^* \quad (113)$$

$$\frac{\partial c_{\mu\omega_1}}{\partial T'} = \beta \frac{\partial^2 c_{\mu\omega_1}}{\partial X^2} + \frac{\beta' \sqrt{R'}}{\sqrt{R''} + \sqrt{R'} R'} \frac{\partial c_{\mu\omega_1}}{\partial R'} + \beta'' \frac{\partial^2 c_{\mu\omega_1}}{\partial R'^2} - \alpha_3 c_{\mu\omega_1}^* \quad (114)$$

$$\frac{\partial c_{\mu\omega_1}}{\partial T'} = \beta \frac{\partial^2 c_{\mu\omega_1}}{\partial X^2} + \frac{\beta' \sqrt{R'}}{\sqrt{R''} + \sqrt{R'} R'} \frac{\partial c_{\mu\omega_1}}{\partial R'} + \beta'' \frac{\partial^2 c_{\mu\omega_1}}{\partial R'^2} + \alpha_4 c_{\mu\omega_1}^* c_{\lambda_2}^* - \alpha_5 c_{\lambda_2}^* c_{\mu\omega_1}^* \quad (115)$$

where

$$\alpha_j = k_j / a, \quad j = 1, 2, 3 \quad (116)$$

$$\alpha_4 = k_4 c_{\lambda_1}^* / a \quad (117)$$

and

$$\alpha_5 = k_5 c_{\lambda_1}^* / a \quad (118a)$$

$$\alpha_6 = k_6 c_{\lambda_1}^* / a \quad (118b)$$

In addition to the initial conditions (41) and (42) we

assume

$$T=0, 0 \leq X \leq 1, 0 \leq R \leq 1, 0 \leq R' \leq 1:$$

$$\begin{aligned} c_{H_2O_2}^b(X, R, 0) &= c_{H_2O_2}^b(X, R', 0) = c_{H_2O_2}^b(X, R, 0) = c_{H_2O_2}^b(X, R', 0) = \\ c_{H_2O}^b(X, R, 0) &= c_{H_2O}^b(X, R', 0) = c_{H_2O}^b(X, R, 0) = c_{H_2O}^b(X, R', 0) = 0 \end{aligned} \quad (119)$$

The boundary conditions include now

$$T' > 0, X=1, 0 \leq R \leq 1:$$

$$c_{H_2O_2}^b(1, R, T') = c_{H_2O_2}^b(1, R', T') = c_{H_2O}^b(1, R, T') = c_{H_2O}^b(1, R', T') = 0 \quad (120)$$

$$T' > 0, X=1, 0 \leq R' \leq 1:$$

$$c_{H_2O_2}^b(1, R', T') = c_{H_2O_2}^b(1, R', T') = c_{H_2O}^b(1, R', T') = c_{H_2O}^b(1, R', T') = 0 \quad (121)$$

$$T' > 0, 0 \leq X \leq 1, R=1:$$

$$c_{H_2O_2}^b(X, 1, T') = c_{H_2O_2}^b(X, 1, T') = c_{H_2O}^b(X, 1, T') = c_{H_2O}^b(X, 1, T') = 0 \quad (122)$$

$$T' > 0, X=0, 0 \leq R \leq 1:$$

$$\left( \frac{\partial c_{H_2O_2}^b}{\partial X} \right)_{X=0} = - \left( \frac{\partial c_{H_2O}^b}{\partial X} \right)_{X=0} \quad (123)$$

$$\frac{c_{H_2O_2}^b(0, R, T')}{c_{H_2O}^b(0, R, T')} = \Theta_{HA/D} S_A(T') \quad (124)$$

(where  $\Theta_{HA/D}$  is defined in analogy to  $\Theta_{A/B}$ )

$$\left( \frac{\partial c_{H_2O_2}^b}{\partial X} \right)_{X=0} = 0 \quad (125)$$

$$\left( \frac{\partial c_{H_2O_2}^b}{\partial X} \right)_{X=0} = - \left( \frac{\partial c_{H_2O}^b}{\partial X} \right)_{X=0} \quad (126)$$

$$\frac{c_{H_2O_2}^b(0, R, T')}{c_{H_2O}^b(0, R, T')} = \Theta_{C/E} S_A(T') \quad (127)$$

$$T' > 0, X=0, 0 < R' \leq 1$$

$$\left( \frac{\partial c_{H_2O_2}^b}{\partial X} \right)_{X=0} = \left( \frac{\partial c_{H_2O_2}^b}{\partial X} \right)_{X=0} = \left( \frac{\partial c_{H_2O}^b}{\partial X} \right)_{X=0} = \left( \frac{\partial c_{H_2O}^b}{\partial X} \right)_{X=0} \quad (128)$$

$$T' > 0, X \geq 0, R=1 (R'=0):$$

$$c_{H_2O}^b(X, 0, T') = c_{H_2O}^b(X, 1, T') \quad (129)$$

$$c_{H_2O_2}^b(X, 0, T') = c_{H_2O_2}^b(X, 1, T') \quad (130)$$



$$c_{\pi}^{\pm}(X, 0, T') = c_{\pi}^{\pm}(X, 4, T')$$

(131)

$$c_{\pi}^{\pm}(X, 0, T') = c_{\pi}^{\pm}(X, 4, T')$$

(132)

$$\left(\frac{\partial c_{\pi}^{\pm}}{\partial R}\right)_{R=1} = \sqrt{\frac{R'}{R}} \left(\frac{\partial c_{\pi}^{\pm}}{\partial R'}\right)_{R'=0}$$

(133)

$$\left(\frac{\partial c_{\pi}^{\pm}}{\partial R}\right)_{R=1} = \sqrt{\frac{R'}{R}} \left(\frac{\partial c_{\pi}^{\pm}}{\partial R'}\right)_{R'=0}$$

(134)

$$\left(\frac{\partial c_{\pi}^{\pm}}{\partial R}\right)_{R=1} = \sqrt{\frac{R'}{R}} \left(\frac{\partial c_{\pi}^{\pm}}{\partial R'}\right)_{R'=0}$$

(135)

$$\left(\frac{\partial c_{\pi}^{\pm}}{\partial R}\right)_{R=1} = \sqrt{\frac{R'}{R}} \left(\frac{\partial c_{\pi}^{\pm}}{\partial R'}\right)_{R'=0}$$

(136)

$T' > 0, X > 0, R = 0:$

$$\left(\frac{\partial c_{\pi}^{\pm}}{\partial R}\right)_{R=0} = \left(\frac{\partial c_{\pi}^{\pm}}{\partial R}\right)_{R=0} - \left(\frac{\partial c_{\pi}^{\pm}}{\partial R}\right)_{R=0} = 0$$

(137)

Now, the set of equations (102)-(115) in connection with the

initial conditions (41), (42) and (119) and the boundary conditions (43)-(50), (54)-(61) and (120)-(137) has to be solved.

After proceeding in the same manner as for the BC mechanism we arrive at

$$\frac{dc_{\pi}^{\pm}}{dT'} \bigg|_{X, R_R} = \text{RHS (88)} - \alpha_2 c_{\pi}^{\pm} c_{\pi}^{\pm} - \alpha_3 c_{\pi}^{\pm} c_{\pi}^{\pm} + \alpha_4 c_{\pi}^{\pm} c_{\pi}^{\pm}$$

(138)

$$\frac{dc_{\pi}^{\pm}}{dT'} \bigg|_{X, R_R} = [\text{RHS (94) without kinetic term}] - \alpha_2 c_{\pi}^{\pm} c_{\pi}^{\pm} - \alpha_3 c_{\pi}^{\pm} c_{\pi}^{\pm} + \alpha_4 c_{\pi}^{\pm} c_{\pi}^{\pm}$$

(139)

$$\begin{aligned} \frac{dc_{\pi}^{\pm}}{dT'} \bigg|_{X, R_R} = & \beta \left\{ -\frac{B_{i,4} \Theta_{\text{eff}} S_2(T')}{A_{i,4} [1 + \Theta_{\text{eff}} S_2(T')]} \sum_{j=2}^{N_{i,4}} A_{i,j} [c_{\pi}^{\pm}(X_j, R_R, T') + c_{\pi}^{\pm}(X_j, R_R, T')] \right. \\ & + \sum_{j=2}^{N_{i,4}} B_{i,j} c_{\pi}^{\pm}(X_j, R_R, T') \left. + \frac{R'}{G_2} \left\{ \sum_{\ell=2}^{N_{i,4}} [I_{\ell,4} (C'_{\ell,4} - C_{\ell,4})] - I_{i,4} C_{\ell,4} - I_{i,4} C_{\ell,4} \right\} \right. \\ & \left. c_{\pi}^{\pm}(X_i, R_R, T') + \sum_{\ell=2}^{N_{i,4}} I_{\ell,4} C'_{\ell,4} c_{\pi}^{\pm}(X_i, R_R, T') \right\} + \alpha_2 c_{\pi}^{\pm} c_{\pi}^{\pm} - \alpha_3 c_{\pi}^{\pm} c_{\pi}^{\pm} + \alpha_4 c_{\pi}^{\pm} c_{\pi}^{\pm} \end{aligned}$$

(140)

$$\begin{aligned} \frac{dc_{\pi}^{\pm}}{dT'} \bigg|_{X, R_R} = & [\text{RHS (92) without kinetic term and } c_{\pi}^{\pm} \text{ substituted for } c_{\pi}^{\pm}] \\ & + \alpha_2 c_{\pi}^{\pm} c_{\pi}^{\pm} + 2\alpha_3 c_{\pi}^{\pm} c_{\pi}^{\pm} - \alpha_4 c_{\pi}^{\pm} c_{\pi}^{\pm} \end{aligned}$$

(141)

$$\begin{aligned} \frac{dc_{\pi}^{\pm}}{dT'} \bigg|_{X, R_R} = & [\text{RHS (160) without kinetic term and } c_{\pi}^{\pm} \text{ substituted for } c_{\pi}^{\pm}, \\ & c_{\pi}^{\pm} \text{ substituted for } c_{\pi}^{\pm} \text{ and } \Theta_{\text{eff}} \text{ substituted for } \Theta_{\text{eff}}] + \end{aligned}$$

$$+ \alpha_2 c_{H_2O}^+ c_{H_2O}^- \quad (142)$$

$$\frac{dc_{H_2O}^+}{dT' / x_i R_0} = [\text{RHS}(94) \text{ without kinetic term and } c_{H_2O}^+ \text{ substituted for } c_{H_2O}^+ c_{H_2O}^-] \\ \text{substituted for } c_{H_2O}^+ \text{ and } c_{H_2O}^- \text{ substituted for } c_{H_2O}^+ c_{H_2O}^-] - \alpha_2 c_{H_2O}^+ \quad (143)$$

$$\frac{dc_{H_2O}^-}{dT' / x_i R_0} = [\text{RHS}(94) \text{ without kinetic term and } c_{H_2O}^- \text{ substituted for } c_{H_2O}^+, c_{H_2O}^-] \\ \text{substituted for } c_{H_2O}^+ \text{ and } c_{H_2O}^- \text{ substituted for } c_{H_2O}^+ c_{H_2O}^-] + \alpha_2 c_{H_2O}^+ c_{H_2O}^- - \alpha_2 c_{H_2O}^+ c_{H_2O}^- \quad (144)$$

$$\frac{dc_{H_2O}^+}{dT' / x_i R_0} = \text{RHS}(93) - \alpha_2 c_{H_2O}^+ c_{H_2O}^- - \alpha_2 c_{H_2O}^+ c_{H_2O}^- + \alpha_2 c_{H_2O}^+ c_{H_2O}^- \quad (145)$$

$$\frac{dc_{H_2O}^-}{dT' / x_i R_0} = [\text{RHS}(94) \text{ without kinetic term}] - \alpha_2 c_{H_2O}^+ c_{H_2O}^- + \alpha_2 c_{H_2O}^+ c_{H_2O}^- \quad (146)$$

$$\frac{dc_{H_2O}^+}{dT' / x_i R_0} = [\text{RHS}(95) \text{ without kinetic term}] + \alpha_2 c_{H_2O}^+ c_{H_2O}^- - \alpha_2 c_{H_2O}^+ c_{H_2O}^- + \alpha_2 c_{H_2O}^+ c_{H_2O}^- \quad (147)$$

$$\frac{dc_{H_2O}^-}{dT' / x_i R_0} = [\text{RHS}(95) \text{ without kinetic term and } c_{H_2O}^+ \text{ substituted for } c_{H_2O}^+] \\ + \alpha_2 c_{H_2O}^+ + 2 \alpha_2 c_{H_2O}^+ - \alpha_2 c_{H_2O}^+ c_{H_2O}^- \quad (148)$$

$$\frac{dc_{H_2O}^+}{dT' / x_i R_0} = [\text{RHS}(95) \text{ without kinetic term and } c_{H_2O}^+ \text{ substituted for } c_{H_2O}^+] \\ + \alpha_2 c_{H_2O}^+ c_{H_2O}^- \quad (149)$$

$$\frac{dc_{H_2O}^-}{dT' / x_i R_0} = [\text{RHS}(95) \text{ without kinetic term and } c_{H_2O}^- \text{ substituted for } c_{H_2O}^+] \\ - \alpha_2 c_{H_2O}^+ \quad (150)$$

$$\frac{dc_{H_2O}^+}{dT' / x_i R_0} = [\text{RHS}(95) \text{ without kinetic terms and } c_{H_2O}^+ \text{ substituted for } c_{H_2O}^+] \\ + \alpha_2 c_{H_2O}^+ c_{H_2O}^- - \alpha_2 c_{H_2O}^+ c_{H_2O}^- \quad (151)$$

Again, the close resemblance of all expressions may be noted.

The current function in this model is determined by the fluxes of A, HA<sup>+</sup> and C to the electrode

$$i = 2 \sqrt{\frac{A}{\pi}} \int_0^A \left[ R \left( \frac{\partial c_{H_2O}^+}{\partial x} \right)_{x=0} + \left( \frac{\partial c_{H_2O}^-}{\partial x} \right)_{x=0} \right] dR \\ = 2 \sqrt{\frac{A}{\pi}} \sum_{j=1}^{N_{H_2O}} Q_j R_j \left[ \frac{1}{1 + \theta_{H_2O} S_A(T)} \left\{ A_{H_2O}^{(j)} \sum_{i=1}^{N_{H_2O}} A_{H_2O}^{(i)} c_{H_2O}^+(x_i, R_0, T') \right. \right. \\ \left. \left. - \theta_{H_2O} S_A(T) \sum_{i=1}^{N_{H_2O}} A_{H_2O}^{(i)} c_{H_2O}^-(x_i, R_0, T') \right\} + \frac{n_2}{n_1} \frac{1}{1 + \theta_{H_2O} S_A(T)} \right. \\ \left. \left[ \sum_{i=1}^{N_{H_2O}} A_{H_2O}^{(i)} c_{H_2O}^+(x_i, R_0, T') - \theta_{H_2O} S_A(T) \sum_{i=1}^{N_{H_2O}} A_{H_2O}^{(i)} c_{H_2O}^-(x_i, R_0, T') \right] \right. \\ \left. + \frac{n_2}{n_1} \frac{1}{1 + \theta_{H_2O} S_A(T)} \left[ \sum_{i=1}^{N_{H_2O}} A_{H_2O}^{(i)} c_{H_2O}^+(x_i, R_0, T') - \theta_{H_2O} S_A(T) \sum_{i=1}^{N_{H_2O}} A_{H_2O}^{(i)} c_{H_2O}^-(x_i, R_0, T') \right] \right] \quad (152)$$

## CONCLUSION

We showed in this paper the use of two-dimensional collocation to spatially discretize partial differential equations describing a model of cyclic voltammetric experiments under the influence of edge effects. The formal similarity of discretized equations for even very complicated mechanisms has been demonstrated by considering the oxidation scheme of phenol 1. This similarity simplifies the writing and testing of computer programs used to calculate numerical simulation results. In fact, a change in mechanism normally only requires the exchange of a few FORTRAN statements while the main body of the program is untouched. We see this as one of the great advantages of our method which outweighs the difficulties encountered while assessing the features and behavior of a new type of a model, as this two-dimensional one. A thorough discussion of the numerical results for cyclic voltammetry simulations is given in part 4.

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